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# Technical Report No. 2

(Contract N6 onr 271 Task Order 18)

## Surface Area of Deep Sea Sediments

Lamont Geological Observatory

(Columbia University)

Palisades, New York

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Task Order 18

Technical Report No. 2

by

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The research reported in this document has been made possible through support and sponsorship extended by the U. S. Navy, Office of Naval Research under Contract N 6 onr 271 Task Order 18. It is published for technical information only and does not represent recommendations or conclusions of the sponsoring agency.

November 1950

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# Surface Area of Deep Sea Sediments

J. Laurence Kulp and Donald A. Carr

## Introduction

The general purpose of the research under Contract N60NR271 Task Order 18, is the absolute age determination of deep sea materials. One of the potentially valuable methods of determining the age of layers of deep sea sediments is the Ionium, or Radioactive Inequilibrium Method, suggested by Wm. Urry. (1) This method is based on the assumption that a constant excess of ionium, (Thorium 230) over the amount in equilibrium with uranium. is incorporated into a sediment of a specified mineralogical type. Thus a plot of ionium content against depth should show the ionium decay curve (half-life, 83,000 years) from which age at a given depth can be calculated.

While direct application of this method to a variety of North Atlantic cores is being pursued, it is essential to understand the mechanism of the ionium incorporation if the limitations of the method are to be defined. For a constant excess of ionium to be present in a sediment, a constant process must be operating in a homogeneous enviroment. While it is reasonable that relative concentrations of ionium and uranium (environment) have remained constant through several hundred thousand years, it is less probable that the physical and chemical characteristics of the sediment have remained invariant. The method obviously will only have validity for a plot of ionium against depth for a given sediment type. Hence the physical and chemical characteristics which may

affect the process must be determined. If the mechanism which produces the excess ionium is adsorption, it is reasonable to assume that the quantity adsorbed might be directly related to absolute surface area. If the type of site required to adsorb an ionium ion can be defined by other experiments, the number of sites available per gram of sediment can be calculated from the surface area.

Further, the surface area of the deep sea sediments may be of considerable value in other types of basic studies of the geology of the ocean bottom. Therefore it was decided to measure the surface areas of a representative suite of specimens from various deep sea cores. The results will be interpreted for their implication to the Ionium Age Method in a later Technical Report when the radioactivity data are completed. This report is primarily concerned with the theory and measurement of surface area.

A brief review of the terms and concept of adsorption may assist in understanding the discussion which follows. If a gas is incorporated in the inside of a solid, it may either dissolve, thus forming a solid solution or it may react to form a compound. In either case it is called absorption. Likewise a gas remaining on the surface of a solid may be attracted slightly in a manner similar to condensation, or it may react chemically with the surface with a much higher bonding energy. The former is called physical or van der waals adsorption while the latter is termed chemical adsorption or chemisorption. The surface area measurement is made by the use of physical adsorption since such adsorption is not selective as to sites above a certain minimum pressure.

When a gas (adsorbate) is admitted to an evacuated solid (adsorbent) some of the gas is adsorbed on the surface of the solid and the rest remains in the gas phase. The relative amounts are determined by the temperature, pressure and nature of the gas and the solid. In physical adsorption, this distribution takes place quite rapidly -- on the order of 15-30 seconds. This type of adsorption will take place between any surface and any gas if the temperature is low enough. A plot of the amount of gas adsorbed against the pressure for a given gas and unit weight of solid at a fixed temperature is called an adsorption isotherm.

Theory

The development of the Brunauer, Emmett, Teller theory of multimolecular adsorption (2) and the previous experimental work and observations on gas adsorption by Brunauer and Emmett (3,4,5) presented chemists with a method of absolute surface area determination of extraordinary versatility. In principle, the method depends on the measurement of the volume of a certain gas required to cover a surface to a depth of a monomolecular layer. Then, knowing the area covered per molecule, it is possible to calculate absolute surface area. The method is simpler to apply and far more accurate than other methods of surface area determination for a fine grained material. Actually it is universal in application both as regards the extent of the surface and the chemical nature of the surface. Absolute values of surface area are probably correct to 20% while relative values obtained with different adsorbent gases at different temperatures agree to within 10%. For a given experimental arrangement, operating with a single gas at a fixed temperature, the reproducibility is 1-2%. In order to obtain the best value for

the actual surface of an adsorbent, the smallest molecules should be used (hydrogen and helium) but since it is necessary to work below the boiling point of the gas, one usually uses argon or nitrogen at liquid air temperatures. The difference in surface area for most materials is certainly not significant.

Numerous minor modifications have been proposed for the BET theory (6,7,8,9) but the absolute surface area is not affected by more than the 20% originally suggested as the limit of absolute error by the authors of the theory. A recent paper by Halsey (10) develops a new theory of physical adsorption on the basis of the non-uniformity of real surfaces. Halsey objects to the untenable hypothesis in the BET theory that an isolated adsorbed molecule can adsorb a second molecule on top, yielding the full energy of liquefaction, and that in turn the second molecule can adsorb a third, and so on. Halsey's reasoning would indicate that below a $p/p_o$ of $\frac{1}{2}$ only a monolayer exists. However Halsey admits the surface area determinations remain completely satisfactory. This is due in part to the fact that for ionic surfaces using a non-polar gas as adsorbent, the heat of adsorption of the first layer is considerably larger than for subsequent layers.

We must now derive the isotherm equation. The basic assumption underlying the theory of multimolecular adsorption is that the forces are van der Waals in character, e.g. those acting in condensation to the liquid phase.

Let $S_o, S_1, S_2 \ldots S_i$ represent the surface area that is covered by $0,1,2 \ldots i$ layers of molecules. If $n_m$ is the maximum number of molecules that are adsorbed on the first layer, then

$$S_0 = \sigma_0 (n_m - n_1)$$
$$S_1 = \sigma_0 (n_1 - n_2)$$
$$S_2 = \sigma_0 (n_2 - n_3) \qquad (1)$$
$$\text{etc.}$$

where $\sigma_0$ is the area per molecule.

At equilibrium the rate of condensation must equal the rate of evaporation for each layer. Hence for the first layer,

$$a_1 p (n_m - n_1) = b_1 (n_1 - z n_2) e^{-E_1/RT} \qquad (2)$$

where p is the pressure, E, the heat of adsorption in the first layer and a, b, and z are constants. Analogous equations can be written for the higher layers.

The left hand side of the equation shows that the rate of condensation is proportional to the pressure and the number of available sites. The right hand side says the rate of evaporation is proportional to the total number of molecules on that layer minus a certain effect produced by the molecules that are covered by two or more layers. The BET theory assumes z=1, i.e. themolecules under a layer or two of molecules can not evaporate through the superimposed layer. Hüttig, on the other hand, (11) uses the other extreme that z = 0, hence he assumes the molecules covered by second and higher layers still play their role as freely as if the higher layers were not present. Probably the true situation is somewhere between these extremes but in the surface area evaluation it is a second order correction on the absolute value as will be indicated below.

We will develop the BET isotherm following Brunauer (12) and then compare the BET and Huttig equations. The Huttig equation may be derived in exactly analogous manner from this point.

If now we multiply (2) by $\sigma_o$ and assume that z equals unity we obtain:

$$a_1 p S_0 = b_1 S_1 e^{-E_1/RT}$$
$$\vdots \qquad\qquad \vdots$$
$$a_i p S_{i-1} = b_i S_i e^{-E_i/RT} \tag{3}$$

Since the total surface of the adsorbent is

$$A = \sum_{i=0}^{i=\infty} S_i \tag{4}$$

and the total volume adsorbed is

$$v = v_o \sum_{i=0}^{i=\infty} i S_i \tag{5}$$

where $v_o$ is the volume adsorbed per $cm^2$ of the surface when covered by a monolayer. It follows that

$$\frac{v}{A v_o} = \frac{v}{v_m} = \frac{\sum_{i=0}^{i=\infty} i S_i}{\sum_{i=0}^{i=\infty} S_i} \tag{6}$$

where $v_m$ is the volume of gas adsorbed when a monolayer is complete.

From the basic assumption of the multimolecular theory

$$E_2 = E_3 = E_4 = \cdots\cdots = E_i = E_L \tag{7}$$

where $E_L$ is the heat of liquefaction;

further, $$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \cdots\cdots = \frac{b_i}{a_i} = g \tag{8}$$

where g is some constant.

In these steps we have assumed that the forces binding molecules in the second and higher layers are simply those of liquefaction. This is reasonable in view of the short range of van der Waals forces.

It is now convenient to express $S_1$, $S_2$ etc. in terms of $S_o$.

$$S_1 = y S_o \quad \text{where } y = (a_1/b_1)\, p\, e^{E_1/RT} \tag{9}$$

$$S_2 = x S_1 \quad \text{where } x = (p/g)\, e^{E_L/RT} \tag{10}$$

$$S_3 = x S_2 = x^2 S_1 \tag{11}$$

$$S_i = x S_{i-1} = x^{i-1} S_1 = y x^{i-1} S_o = C x^i S_o \tag{12}$$

$$\therefore C = y/x = (a_1 g/b_1)\, e^{(E_1 - E_L)/RT} \tag{13}$$

substituting into (6) we obtain

$$\frac{v}{v_m} = \frac{C S_o \sum_{i=1}^{\infty} i x^i}{S_o \left[1 + C \sum_{i=1}^{\infty} x^i\right]} \tag{14}$$

But

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} \tag{15}$$

Also $$\sum_{i=1}^{\infty} i x^i = x \frac{d}{dx} \sum_{i=1}^{\infty} x^i = \frac{x}{(1-x)^2} \tag{16}$$

Now substituting (15) and (16) into (14)

$$\frac{v}{v_m} = \frac{Cx}{(1-x)(1-x+Cx)} \tag{17}$$

At $p = p_o$ on a free surface all layers must be filled

$$\therefore x = 1 \quad \text{or} \quad (p_o/g)\, e^{E_L/RT} \tag{18}$$

Therefore

$$x = p/p_o \tag{19}$$

Substituting (19) into (17) we obtain the isotherm equation

$$v = \frac{v_m C p}{(p_o - p)\left[1 + (C-1)\left(p/p_o\right)\right]} \qquad (20)$$

which may be transformed to

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m C} + \frac{C-1}{v_m C}\frac{p}{p_o} \qquad (21)$$

If $\frac{p}{v(p_o-p)}$ is plotted against $p/p_o$ a straight line should result with a slope equal to $\frac{(C-1)}{C v_m}$ and an intercept $\frac{1}{v_m C}$ . It is therefore possible to determine both $v_m$ and c. The former gives the surface area and the latter the heat of adsorption in the first layer since $E_L$ is known. To a good approximation on most surfaces c is large compared to unity hence to 2% the slope may be taken as the reciprocal of $v_m$. This assumption may easily be checked by measuring the intercept for a few cases.

Reasoning from the Hüttig assumption one obtains in place of (21) the following equation:

$$\frac{p}{v}\left(1 + p/p_o\right) = \frac{p_o}{C v_m} + \frac{p}{v_m}$$

In this equation a graphical plot of $\frac{p}{v}\left(1 + p/p_o\right)$ against p or $p/p_o$ is a straight line with a slope equal to $1/v_m$. The comparison of these isotherms is shown in Figure 1.

Ross (9) shows some adsorption isotherms for ethane on NaCl at liquid oxygen temperatures. Recomputed into the Hüttig equation, a straight line is obtained over a much larger range of $p/p_o$ than the simplified BET equation gives. Ross states that the longer linearity provides greater precision for the method. His data also indicates that

under the conditions he used the surface area values lie within 10% of each other.

Since Halsey has already demonstrated some unreality in one of the assumptions underlying the multimolecular theory (whether BET or Hüttig), it is not profitable to discuss the implications of these differences at length. However it should be mentioned that mere adherence to linearity does not necessarity prove the correctness of the equation. Further it has been noted that the Hüttig equation isn't linear for all types of adsorbents. (13) Representative BET plots for the adsorption of argon on deep sea sediment samples at liquid nitrogen temperatures are shown in Figure 1. The Hüttig plots for the same data are plotted for comparison. Note the tendency of the Hüttig plot to curve at low $p/p_o$ values. Thus Ross' claim to greater precision is questionable for these conditions. Further the fact that the BET equation is linear to lower values of $p/p_o$, would favor the retention of BET surface area values to the Hüttig values. Table 1 shows the comparison of the surface areas obtained for these three samples by the two methods. Generally in this case the Hüttig values lie about 20% higher. Until more conclusive theoretical work is done to establish the best equation for determining absolute surface area values, it is felt best to use the BET for comparison. In any case, the absolute values are probably correct to 20%.

Table 1

| Core Sample | Depth | Surface area in $m^2/g$. BET | Hüttig |
|---|---|---|---|
| A153-141 | 1025 cm. | 5.39 | 6.31 |
| A152-137 | 523 | 25.6 | 31.6 |
| C8 - 7 | 145 | 12.5 | 16.4 |

Apparatus and Procedure

The system (Figure 2) consists of an oil (1) and mercury (2) vacuum pump in series followed by a dry ice trap (3), a MacLeod Gauge (7), an argon manometer (5), adsorption bulb (4), and gas burette (6). Purified tank helium and spectroscopically pure argon are stored in the bulbs above the manifold.

The samples of deep sea sediments were taken from cores obtained by P rof. M. Ewing on recent Atlantic expeditions. Preliminary tests showed a difference in surface area of less than 10% in a sample that was lightly broken up to fit in the adsorption bulb and the same sample after it had been ground to fine powder with a mortar and pestle. The procedure of grinding the sample to pass a 50 mesh screen was adopted as standard since this size proved most satisfactory for alpha counting on the same samples.

The sample weighing about one gram was first heated for two hours at 150° C under vacuum in the adsorption bulb (4). Heating for twelve hours at 280° C produced no change in the surface area. Therefore two hours was adopted at the lower temperature as sufficient to remove all adsorbed water as well as volatile organic impurities from the sample. The ground joint of the adsorption bulb was cooled by a stream of air during the heating to prevent any leakage. After the sample had cooled to room temperature, the entire system was pumped to better than $10^{-5}$mm. Next the "dead space" of (4) is determined by expanding a known amount of helium from the gas burette (6) into the adsorption bulb (4) with the adsorption bulb surrounded by liquid $N_2$. This is repeated three times. The helium is then pumped out of the system and argon admitted to (5) in sufficient quantity to produce a liquid phase with the liquid nitrogen

(4) and (5). The vapor pressure of the argon at this temperature, $p_o$, is read on manometer (5). The adsorption isotherm of argon on the sediment is then determined by expanding successive quantities of argon from (6) into (4). The following relation indicates how the amount adsorbed is determined.

$$P_{\substack{\text{INITIAL}\\(\text{BURETTE})}} V_{\text{BURETTE}} - P_{\text{FINAL}} V_{\substack{\text{DEAD SPACE}\\+\text{BURETTE}}} = P V_{\text{ADSORBED}}$$

The process is continued until the final pressure after adsorption is such that $p/p_o$ is greater than 0.30. (At higher values the simple BET plot is not linear. The volume adsorbed is thus calculated for each final pressure and converted to S.T.P.. Now there is sufficient data in the correct form to obtain the values for $v\sqrt{\frac{p}{p_o - p}}$ and $p/p_o$ so that the BET plot can be made. The reciprocal of the slope is the volume of gas required for a monolayer. The crossectional area for the argon atom is assumed to be 12.9 sq. $A^o$ after Armbruster and Austin (14). Therefore

$$\frac{V_m \times \text{AREA/MOLE} \ (\text{sq M})}{\text{cc./MOLE AT S.T.P} \times \text{SAMPLE WEIGHT}} = \text{SURFACE AREA} \ (\text{sq. METERS/GM})$$

Figure 1 shows the BET plot for three representative core samples. They were chosen to show the considerable range in surface area values. They also show the variation in the precision. The curve for A152-137-523 is typical of a careful measurement without experimental difficulties. This shows the remarkable linearity and the excellent precision obtainable with the method. On the other hand, the curve for C87-145 is about as poor in precision as is tolerable. Even with this spread of points, however the surface area will be correct within 5%.

Results

The BET surface areas of about 80 samples taken from 14 different cores have been measured. These samples were selected to yield information on as wide a range of sediment types as possible. In core A-152-118 a fairly detailed analysis throughout the length of the core was carried out. The results are summarized in Table 3.

In order to compare the surface area of deep sea sediments with other common materials, Table 2 has been compiled. This data was obtained by other workers using the BET technique (12,15). Note the range in surface area from a geometrical area like mica, through ground cement, montmorillonite, illite, silica gel and Darco G. With Darco G almost every other carbon atom is on the surface.

Table 2
Surface Area of Various Substances

| Adsorbent | Surface Area $m^2/g$ |
|---|---|
| Mica (0.1 mm sheets) | 0.0036 (approx. geom. area) |
| $Fe_3O_4$ catalyst (unreduced) | 0.02 |
| $CuSO_4 \cdot 5H_2O$ (40-100 mesh) | 0.16 |
| KCl (finer than 200 mesh) | 0.24 |
| Pumice | 0.38 |
| Cement | 1.08 |
| $BaSO_4$ (pptd.) | 4.30 |
| Montmorillonite and Kaolinite | 15.5 (15.3) |
| Cecil soil 9418 | 32.3 |
| Halloysite | 43.2 |
| Illite | 97.1 |
| Silica gel | 584. |
| Darco G | 2123. |

In Table 3 the columns give, in order, the core number, its location, the depth of water, the point at which it was sampled expressed in cm. from the top, the measured surface area, and a brief description of the core at that point. It is evident that the surface area of the deep sea sediments may vary by a factor of ten. Variations up to 30% occur even in such homogeneous cores as C-8-7. In this core, there is an unconformity at 335 cm. The pink clay below 335 cm. is somewhat finer than the green above and has cold water fauna. The sample taken at 343 cm. contained sufficient sand to lower the surface area over that of the purer pink clay.

Core A152-84 illustrates the sharp contrast in surface area by a calcareous clay with detrital material and cold water fauna and a globigerina ooze which is made up of fairly large foraminifera shells. These shells have essentially no internal surfaces and hence are as effective as rounded sand grains in lowering the surface area of the aggregate.

In core A152-88, a volcanic ash layer at 94 cm. is clearly visible without the aid of a microscope. The surface area is comparatively low for while the surface area of fine volcanic ash must be greater than pumice, it is still glassy and probably have few internal surfaces. At 262 cm. calcium carbonate coccoliths surrounding large forams make up about 85% of the material. While the coccoliths have little internal surface, they are very fine particles. However the forams cause a noticeable reduction in the surface area from that of a pure coccolith ooze.

Core A152-127 is very homogeneous and contains the finest clay observed in these cores. The surface area of 36.7 $m^2/g.$ is correspondingly high.

A152-135 is a core taken at the foot of the Caryn sea mount beyond the continental slope. At 348 cm., it is a silty gray clay with about 20% sand. At 710 cm., however, there is very little sand and not enough foraminifera to appreciable lower the surface area.

A152-137 shows the effect of foraminifera on the color and surface area of the sediment. In general as the concentration of forams increases the color becomes lighter and the surface area decreases. There is a sharp break in lithology at 50cm. The deeper water red clay appear to always have a higher surface area than the green or even the gray clay.

A153-141 is a core of fine deep sea sands. The surface area at 745cm., where the amount of clay is very small, is more than doubled by the presence of about 10% clay at 1025 cm. (The term clay in this discussion refers to texture, not mineral composition. It appears that most of the "clay" of the deep sea cores is rock flour. Kaolinite is rare while illite and montmorillonite are sometimes present in minor amounts.)

A156-12 is a heterogeneous core. At 30cm. there is a sandy layer, at 68 cm. a typical pink clay with some foraminifera and at 308 cm. a clay ball found in a gravel layer in this Hudson Canyon core. This plastic clay is probably continental kaolinite or montmorillonite.

C10-10 shows the low surface area of a chalky layer composed of coarse calcium carbonate Amphistegina mixed with volcanic material.

C10-5 has a texture and composition at 430 cm. similar to C10-10 but at 211 cm. the fine grained coccolithic foraminiferal carbonate sediment is present. Near 100 cm. the core is composed largely of bentonitic material.

A156-2 is of considerable interest in that it is composed of very fine Eocene coccolithic material. This material gave the highest surface area observed in this study.

A rather complete surface area check was made of core A152-118. There is good correlation between the surface area, the type of sediment, the coccoliths and forams present in the relations discussed above. At the top the core is about 60% calcium carbonate, a light pink globigerina ooze with forams not abundant. The surface area is less than that for the pure clay since the clay is diluted with forams. At approximately 30 cm. depth the sediment increases in clay content becoming a darker red (14B7 Ridgeway) and the surface area jumps to 34.1 $m^2/g$. From 50 to 80 cm. the color gradually becomes lighter with shell content increasing. There is a marked change at 80 cm. The color at 108 cm. is (13A3) while the surface area at 110 cm is 21.9 $m^2/g$. From here down to 300 cm. the core is quite uniform with a slight increment in clay content bringing the color to 13B5 at about 225 cm. and giving a surface area of 25 $m^2/g$. at 234 cm. From 300 cm. to 380 the sediment is a deep water red clay with very few forams. The remaining samples were a fairly homogeneous red clay with a few fragmental forams.

A157-5 was also analyzed in some detail. The upper 20 cm. consists of a foraminiferal gray clay with a surface of 18.8$m^2/g$.. Below 20 cm. the foram content drops off markedly but the clay type appears to remain the same. From 75 to 225 cm. the material was inhomogeneous glacial marine sediment. The surface area depended in these samples on the percentage of light tan (continental?) clay. At 248 cm. a gray foraminiferal clay was sampled and yielded a customary value for surface area for this type.

Discussion

These data suggest the general pattern of surface area distribution in deep sea sediment types. While the areas measured range from 2.5 to 40 $m^2/g$. and hence are significantly different, nevertheless they are more uniform than might have been expected. The relatively narrow range compared to materials shown in Table 2 is due to the sorting and sizing occurring in the long transportation process to the open ocean.

From the available data one may generalize the surface areas of certain sediment types. The surface area of fine sand or coarse forams (with minor clay) range from 1-5 $m^2/g$. For the continental slope green clay, the values are from 10-14 $m^2/g$. Sediment made up largely of small forams or of volcanic ash range from 5-10 $m^2/g$. Typical globigerina ooze of foraminiferal gray clay range from 10-20 $m^2/g$. depending on the foram content. The pure gray or light pink deep sea clay appears to have a surface area of about $30\pm5$ $m^2/g$., decreasing with foram content and increasing with ferric oxide content. Fine coccolithic material may reach from 35-40 $m^2/g$. in surface area if pure. The percentage of this material in the ordinary globigerina ooze affects the surface area considerably.

As would be expected, the glacial marine deposits are inhomogeneous and show a wide variation in surface area depending on the selection of the material. It appears that the plastic clay associated with these sediments is continental with a surface area of about 40-50 $m^2/g$.

The range of surface area shown by these materials is such that they could be described as moderately good adsorbents. It is to be expected from the polar nature of the minerals comprising the sediments that the entire surface would be covered by a layer of adsorbed ions. The p articular concentration of a particular ion would be determined by the energy of adsorption

and the relative concentration of that ion in sea water. Since no satisfactory adsorption data is available in the low concentration range of the radioelements in sea water, it is not possible to evaluate the importance of surface area in the precipitation of these ions. If an equilibrium process exists the surface area may be an important variable. However, if it is a rate process and there is more than enough surface on any of these materials to adsorb most of the radioelements, then the extent of surface area has little significance. Experiments are now being conducted in this laboratory to study the adsorption of the radioelements on deep sea sediments.

## Conclusion

The surface areas of a representative set of deep sea sediment types have been determined to within an accuracy of 2%. The values range from 2.5 to 40 $m^2/g$. but are characteristic of a specific sediment type. This information, when coupled with adsorption data, may permit a definition of the mechanism by which ionium is removed from sea water

## Acknowledgement

The authors wish to acknowledge the helpful discussions with Mr. David Ericson on the material of this paper. Mr. Ericson also provided the lithologic description of the cores.

****

Table 3

Specific Surface Areas of Deep Sea Sediments

| Core No. | Depth | Location | Water depth | Surface Area $m^2/g$ | Description |
|---|---|---|---|---|---|
| C-8-7 | 26cm. | 35°56'N,74°41'W | 1370 meters | 10.5 ±0.4 * | Typical green clay |
| | 53 | | | 12.7 ±0.5 | Continental slope |
| | 99 | | | 12.1 ±0.5 * | " |
| | 130 | | | 11.7 ±0.5 | " |
| | 145 | | | 12.5 ±0.5 | " |
| | 188 | | | 10.3 | " |
| | 227 | | | 11.1 ±0.4 | " |
| | 330 | | | 14.0 ±0.5 | " |
| | | (unconformity) | | | |
| | 340 | | | 15.5 ±0.5 | Pink clay similar above |
| | 343 | | | 10.7 ±0.4 | Pink clay with some sand |
| | 361 | | | 17.3 ±0.5 * | Pink clay |
| | 487 | | | 12.6 ±0.5 | " " |
| A152-84 | 100 | 44°21'N,30°16'W | 2750 | 23.6 ±0.7 | Calcareous clay, detritus, |
| | 280 | | | 18.7 ±0.6 | cold water faunal (Wisc.?) |
| | 311 | | | 6.2 ±0.3 | Globigerina ooze, warm |
| | 411 | | | 9.2 ±0.3 | water (Sangamon?) |
| | 450 | | | 10.0 ±0.2 * | " |
| A152-88 | 94 | 39°05½'N,26°25'W | 2380 | 7.1 ±0.3 | Volcanic ash layer |
| | 262 | | | 11.2 ±0.4 | $CaCO_3$ foramnifera and coccoliths |
| | 600 | | | 7.8 ±0.3 | Mostly foramnifera |
| A152-127 | 49 | 34°56'N,46°19'W | 4630 | 29.8 ±0.8 | Pink foraminiferal clay |
| | 270 | | | 30.2 ±0.8 | Gray " " |
| | 649 | | | 36.7 ±0.8 | Red clay |
| A152-135 | 348 | 36°31'N,67°31'W | 4850 | 16.5 ±0.5 | Silty gray clay |
| | 710 | | | 20.8 ±0.6 | Gray clay |
| A152-137 | 18 | 38°05'N,69°35'W | 3800 | 10.2 ±0.4 | Gray foraminiferal clay |
| | 523 | | | 25.6 ±0.7 | Red clay |
| | 630 | | | 24.2 ±0.6 | Red clay breccia (slump?) |
| A153-141 | 745 | 33°26½'N,53°48'W | 5350 | 2.5 ±0.1 | Fine red sand with minor clay |
| | 1025 | | | 5.4 ±0.1 | " |
| A156-2 | 70 | 29°12½'N,76°49'W | 2140 | 38.6 ±0.9 | Fine Eocene coccolith |
| | 172 | | | 36.6 ±0.9 | material ($CaCO_3$) |
| A156-12 | 30 | 38°23'N,70°57'W | 3470 | 4.3 ±0.2 | Sandy layer |
| | 68 | | | 17.2 ±0.5 | Pink foraminiferal clay |
| | 308 | | | 48.0 ±0.9 | Clay ball in gravel (trans.?) |

Table 3

(Continued)

| Core No. | Depth | Location | Water depth | Surface Area $m^2/g$ | Description |
|---|---|---|---|---|---|
| C-10-10 | 182 | 32°19.4'N,64°35.6'W | 1005 | 3.2 ± 0.1 | Coarse $CaCO_3$(Amphistegina) |
| C-10-5 | 115 | 33°37.4'N,62°29.6'W | 2670 | 25.7 ±0.5 | Bentonite,altered ig.rock |
| | 211 | | | 12.5 ±0.4 | Globigerina with coccoliths |
| | 430 | | | 5.0 ±0.2 | Coarse foraminifera. |
| A157-5 | 10 | 48°35'N,36°51'W | 4500 | 18.8 | Foraminiferal gray clay |
| | 23 | | | 27.8 | |
| | 43 | | | 22.5 | |
| | 63 | | | 24.5 | |
| | 84 | | | 28.8 | Light tan clay and sand grains |
| | 112 | | | 32.7 | Blush clay with minor forams |
| | 155 | | | 18.3 | Lt. tan clay & sand silt |
| | 186 | | | 14.2 | Gray clay & forams |
| | 222 | | | 31.1 | Glacial marine clay & silt |
| | 248 | | | 17.8 | Gray foraminiferal clay |
| A152-118 | 11 | 35°07'N,44°40'W | 4340 | 13.4 | Lt. pink globigerina ooze |
| | 25 | | | 17.9 | Increase in clay content |
| | 30 | | | 34.1 | |
| | 40 | | | 29.7 | |
| | 52 | | | 27.1 | Calcareous red clay |
| | 75 | | | 32.5 | |
| | 110 | | | 21.9 | |
| | 128 | | | 25.2 | Gray clayey |
| | 147 | | | 23.3 | globigerina ooze |
| | 150 | | | 21.6 | |
| | 181 | | | 21.7 | |
| | 200 | | | 23.7 | |
| | 210 | | | 24.8 | |
| | 234 | | | 25.0 | |
| | 263 | | | 25.3 | |
| | 285 | | | 22.1 | Gray clayey ooze |
| | 305 | | | 18.0 | |
| | 360 | | | 15.8 | Pink clayey ooze (forams) |
| | 380 | | | 18.8 | |
| | 400 | | | 30.1 | Red calcoreous clay |
| | 407 | | | 24.2 | |

Table 3

(Continued)

| Core No | Depth | Location | Water depth | Surface Area | Description |
|---|---|---|---|---|---|
| A152-118 (Cont.) | 410 | | | 28.4 | |
| | 420 | | | 26.2 | Gray calcoreous clay |
| | 442 | | | 27.6 | |
| | 539 | | | 24.4 | |

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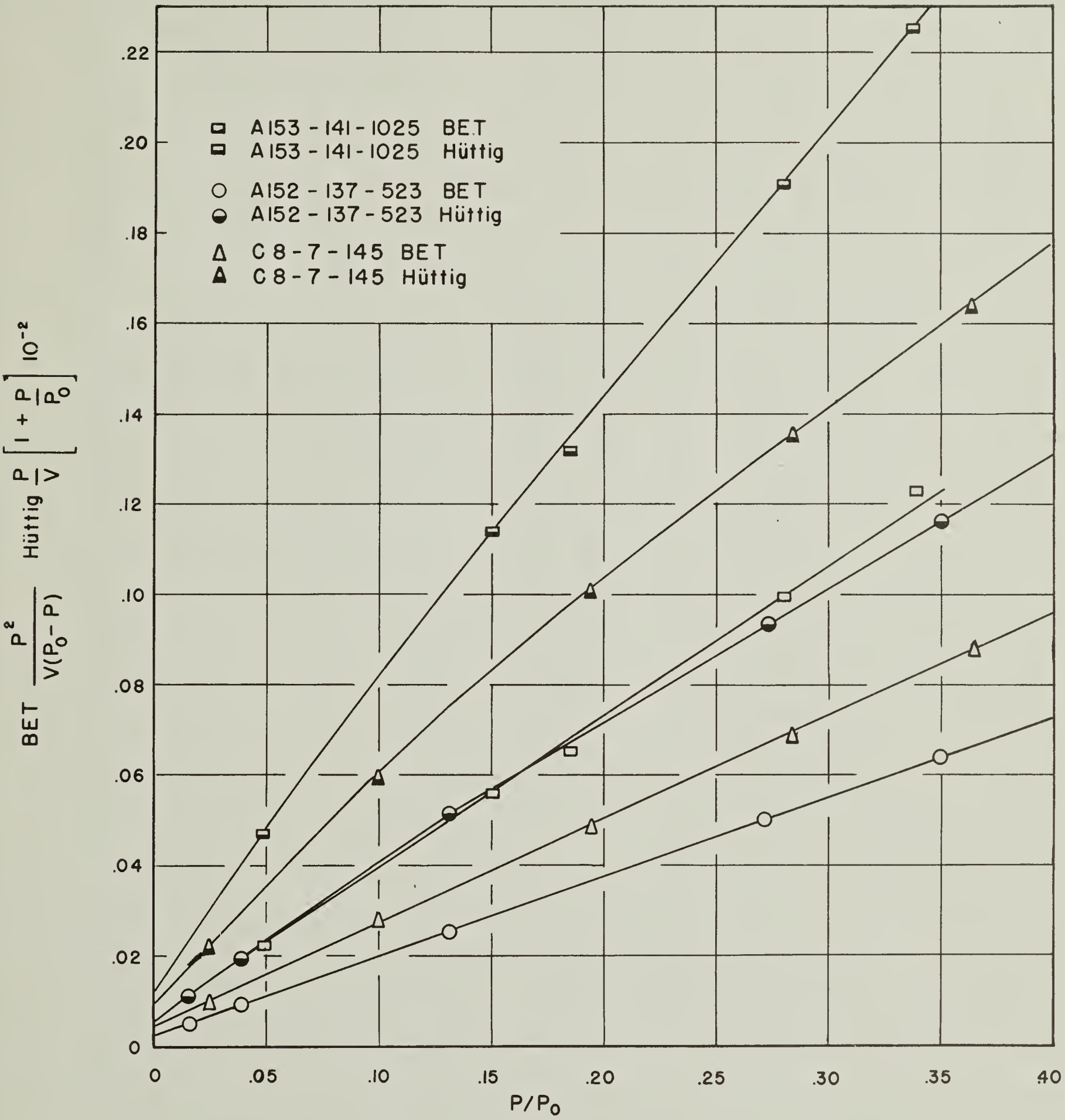


Figure 1. Adsorption isotherm data for three representative core samples plotted according to the BET and Huttig equations.

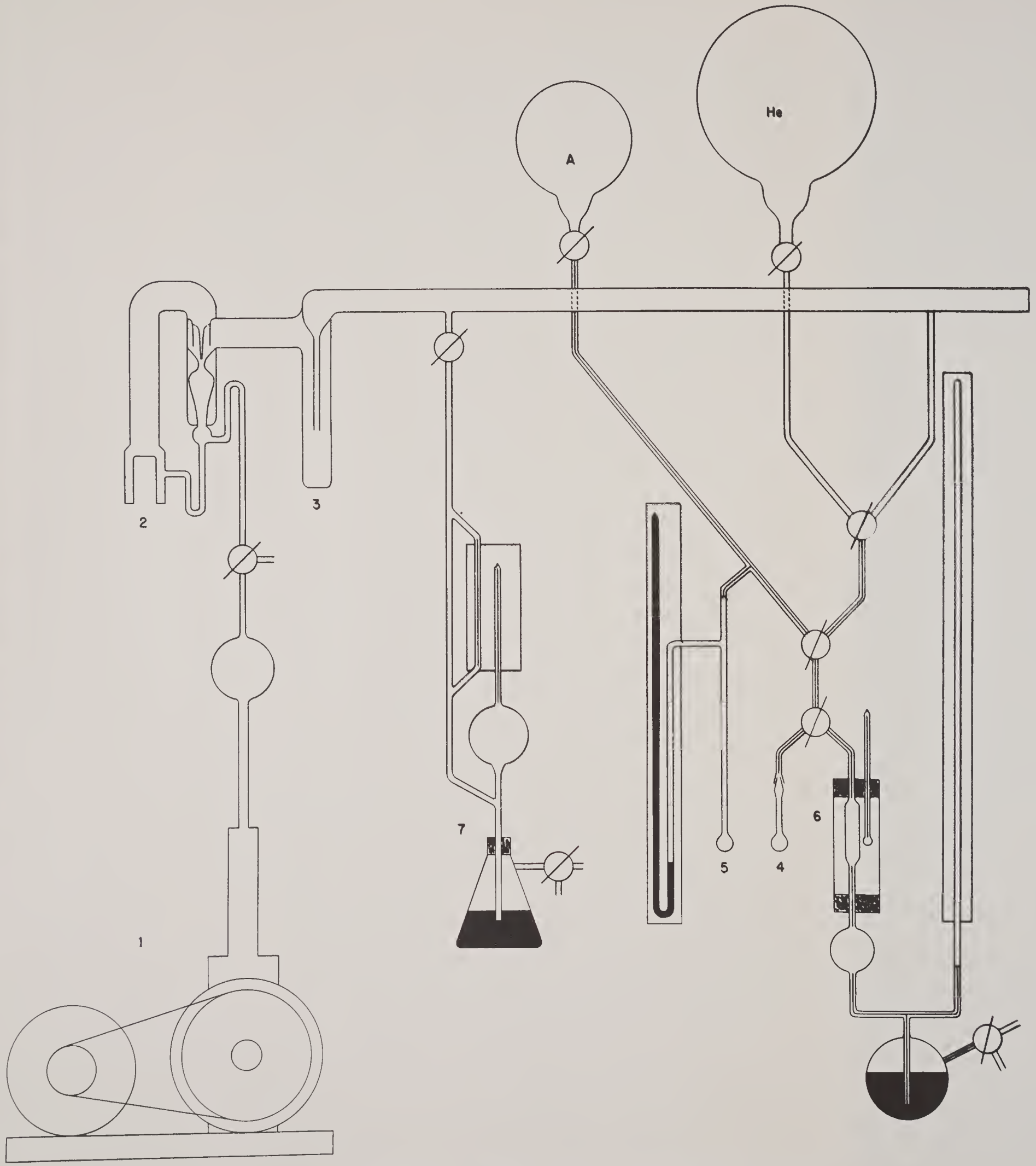


Figure 2. Surface area measurement apparatus.

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